

DISSOLUTION OF SOLID PARTICLES IN GLASS-FORMING MELTS

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Translated from *Steklo i Keramika*, No. 9, pp. 19 – 22, September, 2012.

A generalized analysis of the dissolution of solid particles in glassy melts is performed. Data are obtained on the dissolution kinetics of quartz grains and the kinetic function is determined. The basic directions for enhancing glassmaking are examined.

Key words: melts, dissolution, uniformity, diffusion-boundary-layer, mixing, kinetic function, enhancement of glassmaking.

The molten glass in a glassmaking furnace is obtained from a mixture of different raw materials (batch), which is a statistically disordered state of complete mixing. Initially, the melt obtained from the batch is extremely nonuniform and saturated with bubbles of the gases released and insoluble grains of quartz. Then, together with local physical-chemical processes of the dissolution of quartz mixing of nonuniformities and bubble removal occur. The dissolution of the residual quartz in the melt is a very slow process, taking 60 – 70% of the total time required to make commercial processes. This affects directly the technological uniformity of glass melts. The effect of the presence and character of the nonuniformities on the level of production and the quality of the glass in furnaces with developed convection and a neck is analyzed in [1 – 3]. In [4] it is noted that modern glassmaking furnaces are too inefficient to obtain molten glass with adequate uniformity from the standpoint of satisfying the basic technological principles. This concerns especially the principles of best use of the force driving a process and the energy resources and therefore the principle of technological comparability.

Thus, the acceleration of solid-particle dissolution in glass-forming melts is a topical problem for the glass industry in connection with glassmaking enhancement, improvement of coloring methods, and changing the composition of molten glass by introducing into it appropriate components in a continuous flow.

Let us examine the results of a generalized analysis of solid-particle dissolution in high-viscosity glass-forming melts taking particle size and hydrodynamics into account.

The process of the dissolution of a solid in a liquid medium is described by the equation

$$dm/d\tau = \beta(c_{\text{sat}} - c_{\tau})F, \quad (1)$$

where m is the mass of the dissolve substance, τ the time, β the coefficient of mass transfer, c_{sat} the concentration of the saturated solution, c_{τ} the actual concentration at a given moment, and F the total surface area of the dissolved particles.

The complex heterogeneous processes of solid-particle dissolution in melt, which glass formation during melting and coloring of the molten glass in a continuous flow are, include primarily two stages. Molecular (ion) diffusion through a phase interface and chemical interaction of a solid with the components of the melt occur at the first stage. Removal of the products of dissolution from an interface into the melt interior occurs at the second stage.

To a first approximation the law of concentration variation over the thickness of the diffusion-boundary layer can be regarded as linear [5]. On this basis we can write

$$\beta = D/\delta, \quad (2)$$

where D is the diffusion coefficient and δ is the thickness of the diffusion-boundary layer.

Taking this into account Eq. (1) assumes the form

$$dm/d\tau = D/\delta(c_{\text{sat}} - c_{\tau})F. \quad (3)$$

For spherical particles the dependence of the dissolution rate on mixing in general is determined by the Frössling equation

$$\text{Nu} = 2 + \text{Re}^a \text{Pr}^b, \quad (4)$$

where $\text{Nu} = \beta d/D$ is the Nusselt diffusion number, $\text{Re} = wd/v$ is the Reynolds number, $\text{Pr} = v/D$ is the Prandtl diffusion number, d is the particle diameter, w is the flow velocity relative to a particle, v is the kinematic viscosity and a, b are coefficients.

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The Nusselt number characterizes mass transfer. The Reynolds and Prandtl numbers characterize, respectively, the flow regime and its physical-chemical properties. It should be kept in mind that for dissolution processes the Reynolds number is related with the flow velocity relative to the dissolving particle.

Let us now examine the conditions for natural convection (no mixing) and the possibility of melt motion relative to a dissolving particle due to the difference of the solution and solvent densities. In this case a determining factor is the Grashof number Gr , which can replace the Reynolds number in the dimensionless equation (4):

$$Gr = [(\rho_1 - \rho_2)/\rho_2](gd^3/\nu^2), \quad (5)$$

where ρ_1 and ρ_2 are the density of the saturated solution and the density of the solvent, respectively; g is the acceleration of gravity.

Analysis of the relation (5) shows that under conditions such that fine particles of residual quartz dissolve in a high-viscosity glass-forming melt with a very small density difference $Gr \rightarrow 0$, the Nusselt number in Eq. (4) assumes its maximum value, i.e., $Nu = 2$. On this basis it is possible to calculate the maximum thickness of the diffusion-limited layer:

$$\beta = Nu D/d = 2D/d = D/R, \quad (6)$$

where R is the particle radius.

Combining the relations (2) and (6) we obtain

$$\delta = R. \quad (7)$$

It follows from the relation (7) that for a stationary high-viscosity melt the thickness of the diffusion-boundary layer reaches a maximum and equals in order of magnitude the particle radius. Therefore, Eq. (3) referred to a single particle assumes the form

$$dm/d\tau = D/R(c_{\text{sat}} - c_\tau)F^*, \quad (8)$$

where F^* is the surface area of the dissolving particle.

Substituting in Eq. (8) $F^* = 4\pi R^2$ we obtain the dissolution rate of a particle with radius R :

$$v_1 = dm/d\tau = 4\pi D(c_{\text{sat}} - c_\tau)R. \quad (9)$$

When a particle fragments into N particles with radius r the total dissolution rate of all particles will be

$$v_2 = 4\pi D(c_{\text{sat}} - c_\tau)Nr. \quad (10)$$

When a sphere fragments the volume remains unchanged, so that $4/3 \pi R^3 = 4/3 \pi N r^3$, whence

$$R = r \sqrt[3]{N}. \quad (11)$$

Substituting the expression (11) into Eq. (9) we obtain

$$v_1 = 4\pi D(c_{\text{sat}} - c_\tau)r N^{1/3}. \quad (12)$$

Taking account of Eqs. (10) and (12) the ratio of the dissolution rates is

$$v_2/v_1 = N^{2/3}. \quad (13)$$

This expression gives a relation between the character of the change of the dissolution rates and the degree of comminution of the dissolved particles.

The particle size affects the dissolution rate mainly through the contact surface area and the thickness of the diffusion boundary layer. As particle size decreases the total surface area increases, the thickness of the layer decreases and the coefficient of mass transfer increases in accordance with the expressions (2), (3) and (6). It is desirable to decrease particle size as long as this has a positive effect on the rate of the first stage and the total rate of the overall process. With further comminution the process rate decreases not only because of fine particles clump together into large particles but mainly because the rate of the second stage decreases, i.e., the products of dissolution move into the melt interior.

To determine the effect of mixing on the rate of dissolution it is necessary to take account of the scale of the motion, i.e., the distance over which the velocity of the local flow changes appreciably. The following condition holds for the dissolution of fine particles in high-viscosity melts:

$$d \ll \lambda, \quad (14)$$

where d is the particle diameter and λ is the scale of the motion.

In this case the particles follow the flow and the velocity of the melt flow around the particles goes to zero. The thickness of the diffusion-boundary layer becomes of the same order of magnitude as the particle size and therefore the relation (7) is valid.

In high-viscosity glass-forming melts it is quite difficult to create a regime of developed turbulence ($Re > 10^5$) affecting the thickness of the diffusion boundary layer. Thus, for melt flow during mechanical mixing the modified Reynolds number is given by the expression

$$Re_{\text{mix}} = n d_1^2 \rho / \eta, \quad (15)$$

where n is the rotation frequency and d_1 the diameter of the mixer, ρ is the density of the melt and η is the dynamic viscosity.

For density of the glass-forming melt 2400 kg/m^3 , viscosity $50 \text{ Pa} \cdot \text{sec}$, mixer diameter 0.5 m and mixer rotation frequency 3 sec^{-1} we obtain $Re_{\text{mix}} = 36$. At the same time turbulence starts to develop for $Re_{\text{mix}} > 100$.

When dissolution is intensified by mixing and the condition (14) holds comparative data on the hydrodynamic conditions of dissolution in different assemblies can be obtained from the specific power consumption P on mixing [6]. A. N. Kolmogorov's theory of local isotropic turbulence

gives the theoretical justification for this. Identical hydrodynamic conditions and therefore equal rates of convective diffusion for dissolution of particles with $P_1 = P_2$ and $\beta_1 = \beta_2$ correspond to equal specific powers in two different assemblies with other conditions being equal. Ordinarily, there are no difficulties in calculating the power expended on mixing, so that the data from laboratory experiments can be used to evaluate the conditions for particle dissolution in an industrial assembly.

A generalized analysis of the dissolution of solid particles in high-viscosity melts shows that the dissolution rate will be determined by the rate of transfer of the products of dissolution into the melt interior. Mixing intensifies this stage. To make it more efficient the entire melt volume must be mixed with the flow directions changing. The dissolution rate of particles increases considerably because the particle size decreases, so that as mixing becomes more intense the practical particle size shifts to lower values.

In this connection, mixing-related methods of enhancing glassmaking will be actively developed in the future. This will require new approaches to obtaining experimental data on the kinetics of dissolution of solid particles when designing glassmaking furnaces. In chemical engineering such approaches have been used for a long time for calculating and designing continuous reactors [7, 8]. Specifically, it is shown in [8] that the most convenient kinetic characteristic of the dissolution process is the kinetic function, i.e., the dependence of the fraction of the undissolved component on the dimensionless time at constant temperature and concentration of the active reagent. The dimensionless time equals the ratio of the instantaneous duration of dissolution to the complete dissolution time. A very important property of the kinetic function is its invariance relative to the technological parameters of the process – concentration (composition), temperature and hydrodynamic conditions. The specific nature of the conditions under which the process is conducted is reflected only in the time to complete dissolution. This makes it possible to use data obtained from periodic laboratory experiments to design industrial continuous dissolution processes. Examples of the application of the kinetic function for mathematical modeling of heterogeneous processes of chemical technology are presented in [8].

On this basis experiments were performed on the dissolution of SiO_2 particles during the production of glass with the composition $\text{Na}_2\text{O} \cdot \text{SiO}_2$. The kinetic function for the dissolution of SiO_2 particles in silicate melt is presented in Fig. 1. The figure shows the invariance of the kinetic function relative to temperature. It is obvious that this kinetic function will also be invariant relative to the composition and hydrodynamic conditions. Such kinetic functions can also be obtained for commercial glasses; they can be used to analyze the technological processes involved in glassmaking and new designs of glassmaking furnaces.

Apparently, the future development of glassmaking will be based on glassmaking furnaces with melting tanks con-

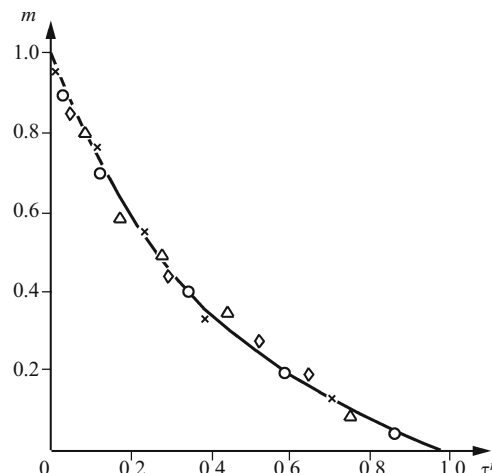


Fig. 1. Kinetic function for the dissolution of SiO_2 particles: \times) 1000°C; \diamond) 1100°C; \circ) 1200°C; \triangle) 1300°C.

sisting of separate standard sections or modules for stage-wise implementation of the process. Definite experience in such implementation of the glassmaking process has been obtained in the production of optical glass [7]. Small tank furnaces consisting of three communicating melting tanks equipped with mixers (for silicate and glass formation, fining and homogenization) are used to melt some forms of optical glass. In the future this experience can be also be used elsewhere in the glass industry where means for enhancing glassmaking are used (high-temperature melting regimes with intensive mixing, use of roof burners, contact combustion of gas in the molten glass and so forth).

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